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# **Bioaccumulation of Heavy Metals in Contaminated River Water-Uppanar, Cuddalore, South East Coast of India**

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Additional information is available at the end of the chapter

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## **1. Introduction**

Industrialization and human activities have partially or totally turned our environment into dumping sites for waste materials. As a result, many water resources have been rendered polluted and hazardous to man and other living systems [1]. The toxic substances discharged into water bodies are not only accumulated through the food chain [2], but may also either limit the number of species or produce dense populations of microorganisms [3]. Aquatic ecosystems are affected by several stresses that significantly weaken biodiversity. River pollution is an environmental problem in the world. They are subjected to various natural processes such as the hydrological cycle occurring in the environment. Because of unprecedented development, human beings are responsible for choking several aquatic ecosystems to death. Storm water runoff and carry out of sewage into rivers are two common ways that various nutrients and other pollutants enter the aquatic ecosystems resulting in pollution [4, 5]. Heavy metal contamination particularly the non-essential elements may have distressing effects on the ecological balance of the recipient aquatic environment with a diverse of organisms including fish. It has particular significance in ecotoxicology, since the heavy metals are highly persistent and have the potential to bio accumulate and bio magnify in food chain, and become toxic to living organisms at higher trophic levels in nature.

Uppanar River is considered to be one of the highly polluted rivers in south east coast of India due to industrialization. SIPCOT (Small Industrial Promotion Corporation of Tamil Nadu, covering an area of about 520 acres with 52 industries) is located on the bank of the Uppanar River at Cuddalore. It was established for chemical, petrochemical, pharmaceutical, biocides, fertilizer, fungicides, chlor-alkai and metal processing industries etc. Many

possible environmental contaminants could be discussed in a review of toxic substances from industrial sources. The combined effect of all these might be the reason of frequent fish death and depletion of aquatic ecosystems in this area. Indiscriminate discharge of partially treated effluents from SIPCOT industrial complex into coastal environment affects both biotic and abiotic system and finally causes some ill effects to human beings through food chain. A detailed study was made on the bio accumulation of heavy metals in the food chain and the spectrum of issues and consequences were discussed in the present study.

The specific objectives of this study are:

- i. The interpretation of the impact of pharmaceutical industrial effluent on surface water quality of Uppanar River in Cuddalore.
- ii. Find out the suitability of river water for fisheries.
- iii. To evaluate the health risk of fish consumption by human beings collected from the river.

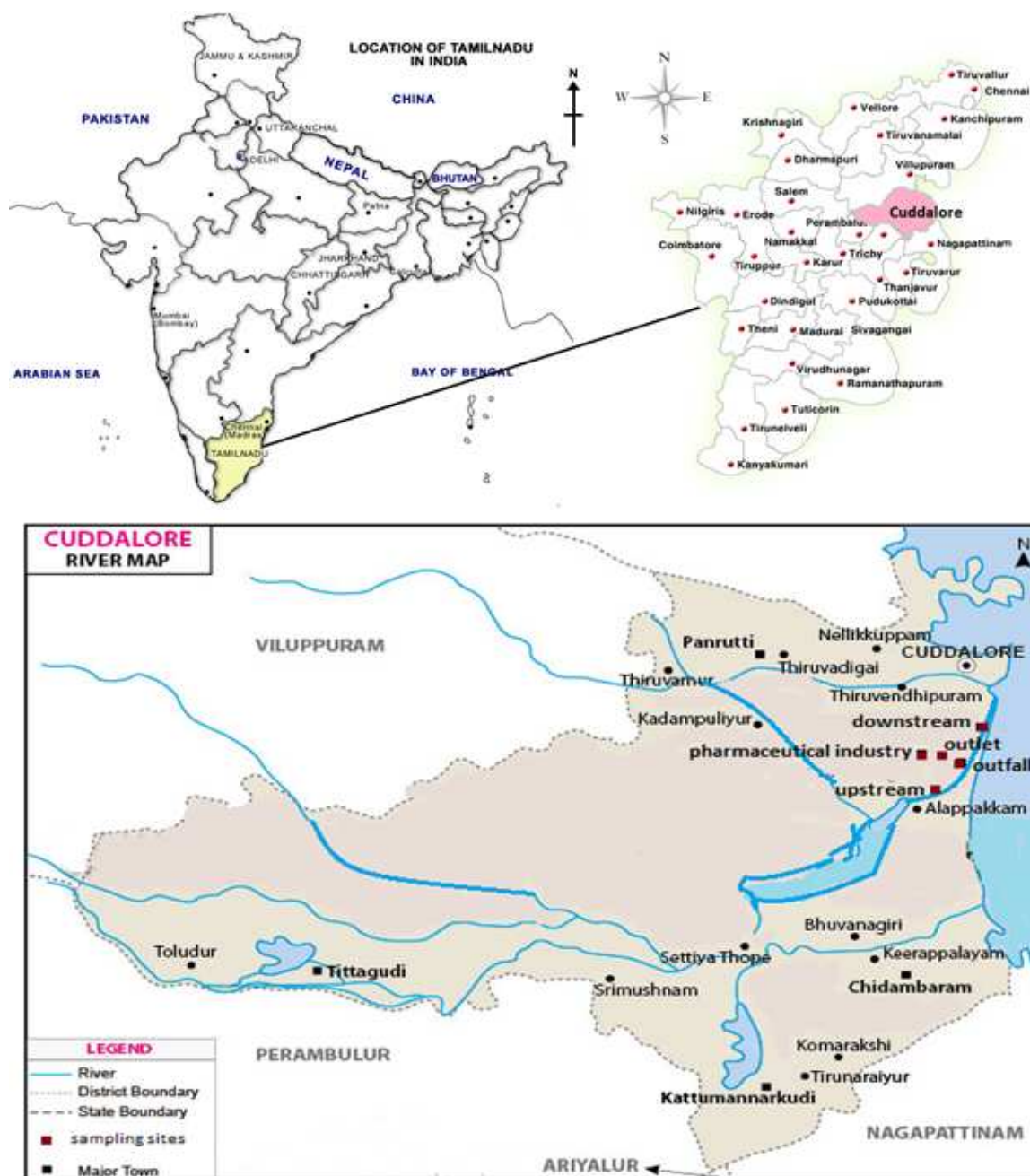
### 1.1. Study area

Uppanar River is a stream in Cuddalore (Lat.11/ 43'N, Long. 79/ 46' E) (Fig. 1). It flows between Cuddalore and Chidambaram Taluks and joins with the Bay of Bengal by the mouth of Gadilam River. It runs behind the SIPCOT (State Industrial Promotion Corporation of Tamil Nadu Limited) industrial complex which consists of Pharmaceutical industries, fertilizers, dyes, chemicals, mineral processing plants and metal based industries. The river receives the partially treated and untreated effluents of these industries through small channels and pipeline. The water at lower reaches is polluted more when compared to the upper reaches. In addition to the industrial wastes, the river also receives the municipal wastes and domestic sewage from the Cuddalore old town. As the river receives the treated and partially treated effluents from nearly 55 industries, it is said to be highly polluted. Pharmaceutical industrial effluent before and after treatment and four stations in the Uppanar River, the river (Outfall), Upstream (uncontaminated -Semmankuppam) and Downstream (Contaminated-Kudikadu) were selected for the heavy metal (Cu, Cd, Mn, Zn and Pb) analyses and seasonal variations were reported. A study on the transfer of Cd, Pb, Cu, Mn and Zn through the food chain of the river Uppanar proved the existence of bioaccumulation in fish.

### 1.2. Sampling methods and sample preparation

Water samples were collected with 1 L polyethylene bottles which were previously cleaned by washing with non-ionic detergent, rinsed with tap water and later soaked in 10% HNO<sub>3</sub> for 24 hours and finally rinsed with deionized water prior to use. During sampling, sample bottles were rinsed with sampled water three times and then filled to the brim at a depth of one meter below the wastewater from each of the four designated sampling points. Temperature and pH measured immediately after collection. The waste water and river water samples were digested and heavy metals were determined

using Atomic Absorption Spectrophotometer (AAS) as described in the APHA standard methods (1992).



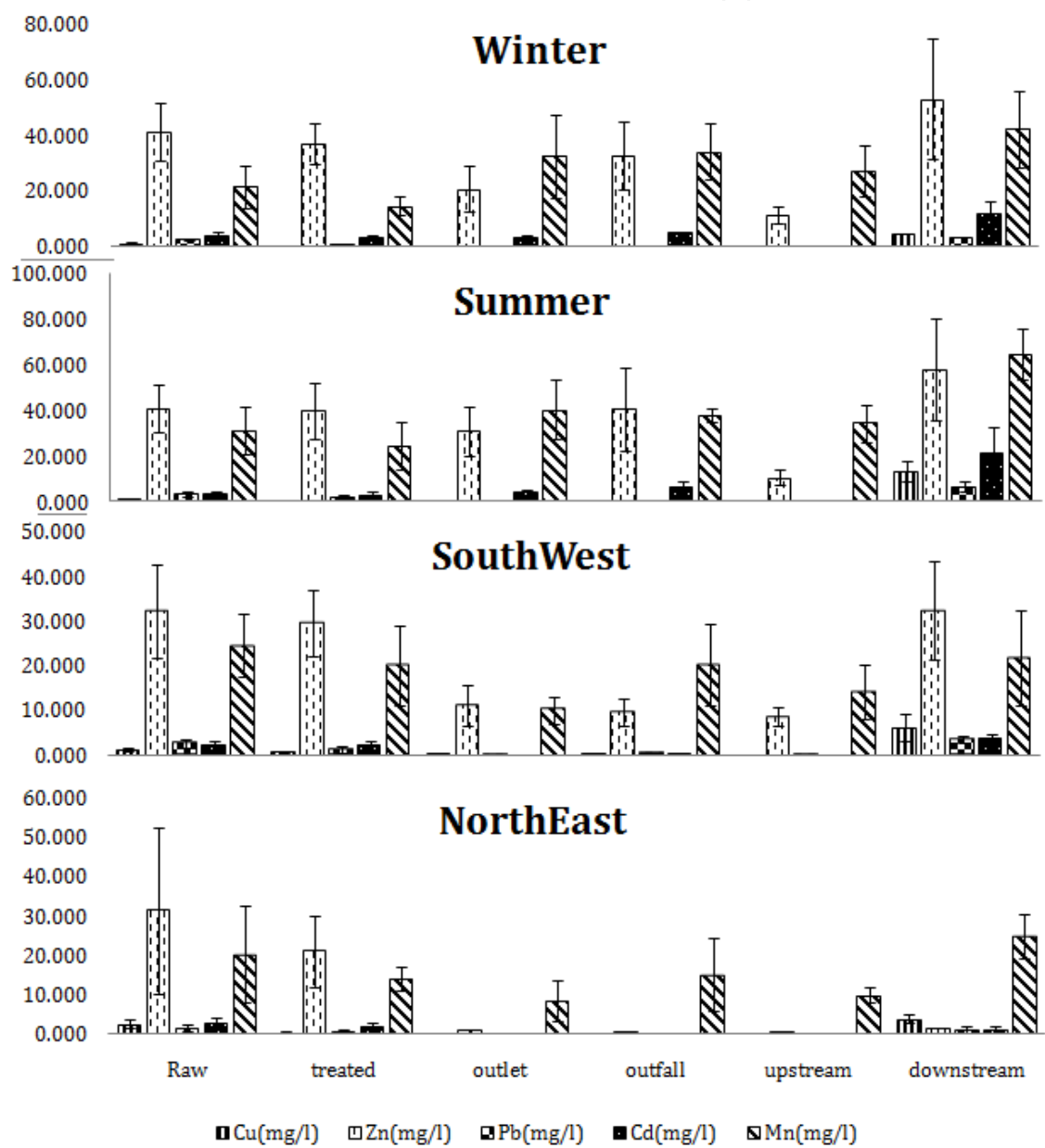
**Figure 1.** The map of Cuddalore and Uppanar River sampling sites

Dried samples of muscle tissues from each fish were digested using microwave digestion system. After digestion, the residues were diluted to 25ml with 2.5% of  $\text{HNO}_3$ . The Instrument (Atomic Absorption Spectrophotometer – AAS) was calibrated with standard solutions and prepared from commercial materials. The water used was deionized and distilled.

The metal analysis of the tissue and water samples (Cd, Cu, Mn, Zn, Pb) were carried out by using Atomic Absorption Spectrophotometer (AAS).

1.3. Result and discussion

The spatial variation of the heavy metals, Cd, Cu, Pb, Zn and Mn) along the six sampling locations of all the four seasons was shown in Fig 2. The average mean concentrations of Cd, Cu, Pb, Zn and Mn were higher in the untreated effluents than the treated effluents.



**Figure 2.** Mean and S.D of heavy metal (Cu, Pb, Cd, Mn and Zn) concentrations in pharmaceutical industry effluents(Raw & Treated) and Uppanar River water at four sampling sites



## 1.4. Cadmium

Cadmium concentrations in unpolluted natural waters are usually below 1 µg/l. Contamination of drinking-water may occur as a result of the presence of cadmium as an impurity in the zinc of galvanized pipes or cadmium-containing solders in fittings, water heaters, water coolers and taps. Drinking-water from shallow wells of areas in Sweden where the soil had been acidified contained concentrations of cadmium approaching 5 µg/l. In Saudi Arabia, mean concentrations of 1– 26 µg/l were found in samples of potable water, some of which were taken from private wells or cold corroded pipes (Mustafa et al., 1988). Levels of cadmium could be higher in areas supplied with soft water of low pH, as this would tend to be more corrosive in plumbing systems containing cadmium. In the Netherlands, in a survey of 256 drinking-water plants in 1982, cadmium (0.1–0.2 µg/l) was detected in only 1% of the drinking-water samples. Cadmium has been shown to induce carcinogenesis by both the inhalation and parental routes of exposure. The variations in the heavy metal concentration of both the untreated and treated effluents were due to the heavy metal decreasing efficiency of primary and secondary treatment of the Effluent Treatment Plant (ETP). The average mean concentration of Cd at the river water ranged from (0.011 – 21.213 ppm) during all the four seasons. There was a higher fluctuation in the various sampling sites of river, which was attributed to the reason of the other industrial and anthropogenic sources. Upstream Cd concentration during all the four seasons were several times lesser than the Cd concentration of raw effluent, which indicated the dilution effect of the river weather and also it showed that this site is free from anthropogenic inputs, and only the natural effects are the predominant factors in this particular site.

### 1.4.1. Copper

Copper is a natural element which is widely distributed in soils, rocks and in rivers and the sea. The Cu is widely used in society and yet is potentially quite toxic to life in rivers. The present result of average mean concentration of Cu at the various sampling stations of river water ranged from 0.230 – 13.313mg/l during all the four seasons. The Cu concentration at outfall increased two folds compared to the outlet that could be attributed to the reason of anthropogenic activities, agriculture runoff, sludge from publicly-owned treatment works (POTWs) and municipal and industrial solid waste dumped into the river water. Copper is released in to water as a result of natural weathering of soil and discharges from industries and sewage treatment plants [7, 8]. The Cu concentration in downstream were several folds higher than the raw effluent Cu concentration. It may be attributed to domestic sewage and run-off from extensive farmed areas [9]. Copper compounds which are used in electroplating industries such as cupric sulphate and cupric acetate and in fertilizers such as copper naphthenate and paint industries such as cuprous oxide, Ceramics and glass industries such as cupric acetate, cuprous and cupric oxides used as pigments and for making glazes were discharged through the treated industrial effluents. Other than this copper released through the domestic activities such as human wastes flushed through the toilets, washing and bathing water etc. Copper occurs naturally in all foods and water and, in small concentrations, plays an essential role in the human diet. Copper in the dissolved form is potentially very

toxic to aquatic animals and plants, especially to young life-stages such as fish larvae. The toxicity of copper is however greatly reduced when it is bound to particulate matter in the river water and when the water is hard. The industries and public should recognize the need to monitor the concentrations in discharges and in rivers closely, to ensure that Water Quality Objectives are not exceeded.

#### 1.4.2. Lead

Exposure to lead causes a variety of health effects, and affects children in particular. Water is rarely an important source of lead exposure except where lead pipes, for instance in old buildings, are common. Removal of old pipes is costly but the most effective measure to reduce lead exposure from water. The higher concentration of Pb at various sampling sites of river water could be attributed to the reason of less soluble of Pb containing minerals in natural water and its concentration diluted through the dilution effect of the water [10, 11]. The Pb concentration in downstream of all the four seasons was several folds higher than the raw effluents. The profile of the Pb showed that it did not have only one source; furthermore higher concentration of Pb in the downstream indicated the presence of contamination through various industrial effluents of SIPCOT area and local anthropogenic inputs. Lead is rarely found in source water, but enters tap water through corrosion of plumbing materials. The most common problem is with brass or chrome-plated brass faucets and fixtures which can leach significant amounts of lead into the water, especially hot water. Most industrially processed lead is applied for fabricating computer and TV screens. The lead compound tetra-ethyl lead is applied as an additive in fuels. This organic lead compounds is quickly converted to inorganic lead, and ends up in water, sometimes even in drinking water. Fortunately, this form of release of lead is less and less abundant. Lead accumulates in leg tissue. The most severe type of lead poisoning causes encephalopathy. Lead toxicity is induced by lead ions reacting with free sulfhydryl groups of proteins, such as enzymes. These are deactivated. Furthermore, lead may interact with other metal ions.

#### 1.4.3. Zinc

Zinc can be introduced into water naturally by erosion of minerals from rocks and soil; however since zinc ores are only slightly soluble in water. Values of 5–22 mg have been reported in studies on the average daily intake of zinc in different areas. The zinc content of typical mixed diets of North American adults varies between 10 and 15 mg/day. Drinking-water usually makes a negligible contribution to zinc intake unless high concentrations of zinc occur as a result of corrosion of piping and fittings. Under certain circumstances, tap water can provide up to 10% of the daily intake (WHO). High natural levels of zinc in water are usually associated with higher concentrations of other metals such as lead and cadmium. Mostly, the zinc is introduced into water by artificial pathways such as by-products of steel production or coal-fired power stations, or from the burning of waste materials. Zinc is also used in some fertilizers that may leach into groundwater. Older galvanized metal pipes and well cribbings were coated with zinc that may be dissolved by soft, acidic waters. Zinc is an essential nutrient for body growth and development; however drinking water containing high

levels of zinc can lead to stomach cramps, nausea and vomiting. Although the Zn is normally found in little amount in nature, it is also emitted through effluents of many commercial industries during mining and smelting (metal processing) activities. In the present study upstream Zn concentration during all the four seasons was several times lesser than the Zn concentration of raw effluent, which showed that there was no adverse effect of effluent on the upstream. The Zn concentration in downstream ranged from 1.130 – 58.046 mg/L of all the four seasons which was attributed to the greatest frequency of near source areas like hazardous waste sites and the release of industrial effluents through the transmission of iron pipes. Urban runoff, mine drainage, and municipal sewages are the more concentrated sources of zinc in water.

#### 1.4.4. Manganese

The element manganese is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans. Industrial emissions containing manganese oxides are the principal source of manganese in the atmosphere. The total atmospheric emission of manganese from anthropogenic sources in India was estimated to be 1225 t in 1984; 78.5% of this originated from industrial processes, mainly related to metal alloy production. Emissions stemming from gasoline-powered motor vehicles accounted for a further 17.2%, whereas the remaining 4.3% of atmospheric manganese emissions were due to the burning of coal for power generation, solid waste incineration and pesticide application. In the present study the Mn concentration in downstream ranged from 21.736 – 64.837 mg/L of all the four seasons and it was several folds higher than the raw effluent, which could be attributed to the reason of its usage in the cleaning, bleaching, manufacturing of iron, steel alloys, batteries, glass and fireworks industries and improper discharge of the effluents from these industries [12,13]. Manganese is an essential element in humans and animals, functioning both as an enzyme co-factor and as a constituent of metalloenzymes. Gross deficiencies of manganese have never been observed in the general population, but a recent experimental study involving human subjects fed a manganese-deficient diet (0.11 mg/d) resulted in the development of dermatitis and hypocholesterolaemia and elevated concentrations of serum calcium and phosphorus. A statistical analysis of the metabolic studies showed that a daily manganese intake of approximately 5 mg is required to consistently maintain a positive balance.

The present results showed that the metal concentration decreased in the ranking order of Zn>Mn>Cu>Cd> Pb during all the four seasons. According to the seasons, it was in the following ranking pattern summer>winter>Southwest>Northeast.

Most of the dissolved heavy metals showed high concentrations during the summer period than that of the other seasons. ANOVA of the results showed that the metal concentrations were significantly different between sampling stations and the four seasons. The highest flows occurred during the northeast monsoon from October to December. It was also observed that for all (five) metals studied; there was a trend of increasing concentrations from the upstream stations to the downstream stations.



2. Bio concentration factor

A study on the transfer of Cd, Pb, Cu, Mn and Zn through the food chain of the river Uppanar proved the existence of bioaccumulation in fish. The Bio- concentration factor of the heavy metals in muscle tissues of fish from the river water are presented in Table 1. The BCF of Cu ranged from 0.001 to 0.009, that of Pb ranged from 0.061-0.100, Cd from 0.003-0.004, Zn from 0.031-0.083, and Mn 0.408-0.922. The BCF value of Cu was found highest (0.009) in *L. calcarifer* and it was low in *A. thalassinus* (0.001), while the BCF value for Pb was highest (0.100) in *M. cephalus* and was lowest in *L. calcarifer* (0.061). The BCF value of Cd was highest (0.004) in *T. mossambica* and *M. cephalus* (0.004) and it was low 0.003 in *A. thalassinus* and *L. calcarifer*. The BCF value of Zn was highest (0.083) in *A. thalassinus* and was lower (0.031) in *L. calcarifer*. The BCF value of Mn was highest (0.922) in *T. mossambica* was highest and was lower (0.408) in *L. calcarifer*. The trends of BCF for heavy metals in four species of fish were in the ranking order of Mn>Pb>Zn>Cu>Cd.

BCF	<i>L.alcarifer</i>	<i>M.cephalus</i>	<i>A.thalasinuss</i>	<i>T.mossambica</i>
Cu muscles/Cu water	0.009	0.002	0.001	0.002
Pb muscles/Pb water	0.061	0.100	0.063	0.074
Cd muscles /Cd water	0.003	0.004	0.003	0.004
Zn muscles/Zn water	0.031	0.041	0.083	0.073
Mn muscles/Mn water	0.408	0.798	0.707	0.922

BCF =Conc. in muscle tissues of fish (dry weight basis) / Conc. in water of the river

Table 1. Bio concentration factor of heavy metals in muscle tissues of fish from the river water

Due to the improper discharge of partially treated industrial waste water and domestic sewage water into the Uppanar river, the level of heavy metals recorded in water of the downstream and the heavy metals other than Zn and Mn in the water of upstream were generally high and their values exceeded the maximum permissible limit when compared with the limits of WHO (Pb – 0.05, Cd 0.005, Zn 5.0, Mn 0.1, mg L<sup>-1</sup>) for drinking water. This situation has arisen as a result of the rapid expansion of industrial activities, followed by increased urbanization and growth of population with exploitation of natural resources, extension of modern agricultural practices as well as the lack of environmental regulations [14]. The present finding showed significant co-relationships between heavy metal concentrations of water and that of the fish tissue, which may indicate that the fish bio-accumulated these elements from the water of Uppanar River. Further, these present result showed that metal concentrations in muscle tissue were below the allowable concentration and consumption safety tolerance in fish set by countries elsewhere, and suggested by WHO. The maximum levels permitted for fishes are - Zn 100, Cu 30, Mn 1.0, and Pb 2.0, µg g<sup>-1</sup> as per WHO and permitted level Cd is 0.05 – 0.1 µg g<sup>-1</sup> [14], None of the metals in the present results were above the prescribed limits; thus have, little threat to public health. The present study indi-

cates that, consumption of these species is safe. However, it is quite evident that there was bioaccumulation of heavy metals in fish tissues and condition may get worse. Therefore, a regular monitoring of heavy metal levels in fishes is necessary.

### 3. Heavy metal concentration of Indian rivers

The comparison of dissolved metal concentration of River Uppanar with other Indian rivers showed that the Cd, Cu and Pb concentration was several times higher than the Achankoil, Ganga, Brahmani and Mahanadi River (Table 2). The comparative results showed Uppanar River is highly contaminated with industrial effluents discharge, which are the important point sources of toxic heavy metals like Cd, Cu and Pb. The concentration of Zn and Mn at Uppanar River was higher when compared to Mahanadi, Ganga and Brahmani, while it was several hundred times higher than Achankoil River [15, 16, 17, 18 and 19]. The present study revealed that pollutants found in river water are also present in pharmaceutical industrial effluents at higher frequencies of occurrence and concentration. Therefore, pharmaceutical industrial ETPs are clearly a significant point source for organic pollutants in surface waters.

Rivers	Cd	Cu	Pb	Zn	Mn	References
Mahanadi River	-	5.9	2.68	11.0	96.9	Kanhauser et al., (1997)
Achankovil River	6.0	224	72	415	699	Prasad et al., (2006)
Ganga River	5	10	120	60	260	Aktar et al., (2010)
Damodhar River	300	3950	-	-	-	Chatterjee et al., (2010)
Brahmani River	4.0	4.7	27	80.1	102	Reza et al., (2010)
Uppanar River	36.08	191.5	98.5	201.38	273.93	Present Study

**Table 2.** Comparison of dissolved metal concentration with other Indian River ( $\mu\text{g/L}$ )

### 4. Conclusion

As heavy metals are not decomposed biologically, level of these metals, beyond recommended limit, may exist in the river for quite a long distance and it may lead to the long term health-related problems to the people and communities using the water, particularly as a domestic supply source. The result of this work revealed that the mean level of heavy metals discharged into the river has exceeded the maximum permissible limit set by Indian Standards for Drinking Water. The resulting effect is the increase in background level of all the pollutants along the river. It is also observed that level of pollutants in the river during summer season is relatively higher when compared to the other seasons. When the quality of the river is compared with the Indian Standards recommended limits for source of water supply, the river was found to contain some heavy metals above the recommended limits,

indicating pollution. Land-use changes in recent years have resulted in a significant deterioration of the water quality of the Uppanar River. Considering the fact that this area is highly populated with many industries and the final drainage of this river ends into the sea, the water quality and pollution status of this river system is of great concern. Therefore, in this study water samples that were taken during four consecutive seasons confirmed that the river has seriously been polluted with Cu, Pb, Mn, Zn and Cd. The result demonstrated that trace elements have originated from various pollutant sources; however, the main anthropogenic sources were industrial wastes, municipal wastes and run-off from agricultural fields.. Heavy metal concentration found in the edible part of fish species are within the WHO permissible limits for human consumption. Thus, there appears to be no immediate threat to the fisheries of the river due to heavy metal contamination. Though, the results indicate that the heavy metal contamination of the river affects the aquatic life including the fish, a scientific method of detoxification of the river water is essential to improve the health of these fish and in turn, the human beings consuming the fishes of the river. Despite mounting urban sprawl of Cuddalore old town in the past decade increased industrialization consequently followed by releasing of untreated industrial effluents into the river played a significant role in polluting the Uppanar River.

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